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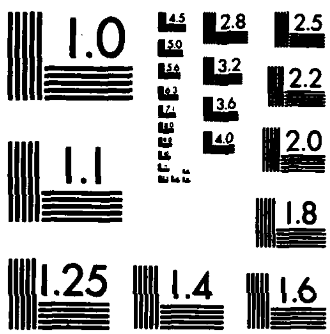

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AD-A136017

- PHASE II REPORT -

EVALUATION OF NRL GLASS

FOR FIBER OPTICS

NRL CONTRACT NO. N00173-78-C-0242

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C. E. Schott

January 15, 1983

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OWENS-ILLINOIS

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ABSTRACT

This report covers a Phase II activity to develop glasses for medium loss fiber optic waveguides. The requirements of the final fiber are that it should have: (1) a diameter of 75 to 125μm with a 50 to 75μm core; (2) a numerical aperature of 0.4 to 0.6; (3) losses of approximately 100dB/km; and (4) radiation resistance.

The Phase II activities include the development of improved cladding and core glass compositions, raw material procurement and batch preparation of high purity materials, controlled atmosphere melting, preparation of preform assemblies, and fiber drawing.

The Phase I activities included the evaluation of a special NRL core glass composition, development of several promising clad glasses and fabricating a test fiber utilizing one of the clad glasses over the NRL core. The Phase I activities are described in "Interim Report - Evaluation of NRL Glass for Fiber Optics", dated 14 September 1979, under the above Contract Number.

A

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

The objective of this program is to advance the development of a special NRL core glass composition and to design a clad glass that has properties which match important corresponding properties of the core so that the pair will perform as functional fiber waveguides. The fibers are intended to have a numerical aperture (NA) greater than 0.4 with potential for moderate loss applications and exhibit improved resistance to intense radiation.

Phase I work was started October 1978, and continued through June 15, 1979. The NRL composition was determined to be suitable for large scale melting activity. Several promising clad compositions were identified and one borosilicate was converted into a test fiber as the cladding over the NRL core. Fiber strength limitations indicated the need for better clad glass stability at the draw temperature and an improved property correspondence to the core glass. A lower melting temperature was also desired for the clad glass so that controlled atmosphere melting could be safely performed in special types of melting units. A Phase II program was recommended to complete development and provide suitable fiber for radiation test purposes.

Phase II work was started September 1979 and continued through December 1980. Additional clad melts were identified as having some of the desired properties. These glasses, however, did not have indices low enough to produce a numerical aperature (N.A.) approaching 0.6 with the NRL core glass. Core glass melts were made in an effort to raise the core glass

index. An improved core glass and clad glass were selected as the "best combination" to achieve desired glass properties and the highest possible N.A. These glasses were melted in a mini-melter under highly reducing conditions and subsequently fabricated into preforms drawn into a test fiber.

Clad fibers were sent to NRL for evaluation. The NRL evaluation was inconclusive due to the brittleness and poor transmission of the fibers. O-I believes the brittleness and poor transmission were due to a poor interface between the clad and core glasses. The brittleness may have been accentuated by the thermal expansion mismatch between the glasses. The poor interface was related to the problem of properly polishing very small preforms.

Recently, in work unrelated to this contract, O-I has found they can produce water white NRL glass in rods one to one and a half inches diameter by about twenty inches long. Further, it appears that commercial N-51A (N_d 1.50) Kimble tubing may be usable as a cladding glass to give a waveguide with N.A. of 0.50.

II. RESULTS AND CONCLUSIONS

1. Improved cladding glasses in the silicate system were identified having indices that yield a numerical aperture as high as 0.54 over a 1.58 N_D glass (NRL) and 0.59 over an improved core glass with N_D of 1.60. However, the high N.A. could not be achieved because many of the clad glasses did not meet other property requirements.

2. Improved core glasses ($N_D \geq 1.60$) were identified in an attempt to gain as high N.A. as possible. Again, many of these glasses could not be considered because of other undesirable properties. An N.A. of 0.6 is not possible when various substitutions are made for CaO or Al_2O_3 in a core glass having a refractive index of 1.60 or lower.

3. The best cladding glasses developed under this study were GS442 and GS451. The best core glasses were the NRL and GS443. The selected combination for the final melting and fiber drawing was GS442 clad over GS443 core. This best combination gave a numerical aperture of 0.47. The selected core glass (GS443) was found to be sensitive to phase separation after the final melts were made and nearly on-target levels of B_2O_3 obtained.

4. An improved cladding glass such as those developed in this study, under proper conditions, can be applied over an improved core glass developed in this study or the NRL core glass.

5. Iron levels of ≈ 8 ppm were analyzed in glasses prepared with in-house normal high purity batch materials. A GS443 core glass melt prepared with the very high purity raw materials was analyzed at < 2 ppm iron.

6. The in-house grinding and polishing capabilities were not adequate to produce sufficiently good preform surfaces to yield a fiber with a good interface. Acid polishing of the preform surfaces with the solutions tried degraded rather than improved those surfaces.

7. Continuous waveguide fibers were produced by a single-draw process. Preforms were fabricated with a 5/8" O.D. and drawn directly to the final diameter.

8. Leaks occurred in the platinum mini-melter followed by subsequent catastrophic failure of the platinum during the sixth melt. Exact cause was not determined, but is thought to have been caused by the CO/CO_2 atmosphere and/or residual organic material in the high purity MOD batch materials.

9. NRL evaluation of the fiber was inconclusive due to brittleness and poor transmission.

10. Recent work indicates that solution of these problems may be feasible.

III. RECOMMENDATIONS

1. The improved core glasses, such as GS443, should be modified to eliminate phase separation.

2. A test fiber using the NRL core glass and the best cladding glass developed to date (GS442) should be tried. The N.A., however, would only be 0.4.

3. Techniques to improve the polish on the surfaces of the clad/core assembly need to be considered.

4. The effect of the reducing atmosphere (CO/CO_2) alone and in combination with high purity MOD materials on the platinum melter needs to be resolved.

5. Additional effort utilizing the NRL core glass and N51A cladding glass should be undertaken. The N.A. would be 0.5.

IV. TECHNICAL DISCUSSION

1. Cladding and Core Glass Modifications

The initial thrust of the composition work under Phase II was to improve the cladding glass. The objectives were to lower the thermal expansion; lower high temperature viscosity while raising the low temperature viscosity to achieve a closer annealing point with the core glass resulting in minimum seal stress; and increase glass stability and Redox stability. A primary goal was to achieve the highest possible N.A. while still maintaining all of the above desirable characteristics. After initial work on cladding glasses only, we believed a different approach was necessary to achieve all of the desired objectives. The new approach was to use the original NRL core composition as the basis for adjusting properties to derive a core glass with somewhat higher index as well as to develop the corresponding clad glass with substantially lower index. By starting with the original NRL glass for matching core and clad compositions, we could achieve the desired numerical aperture (0.4 minimum) and other physical properties and in addition achieve important relatively low melting characteristics for use in our existing melting apparatus.

1.1 Cladding Glass Modifications

The basic NRL core glass was modified in various ways to decrease the index of refraction for use as a cladding glass. Each of these series of modifications will be discussed separately below. The general idea for substitution of ions in these glasses is analogous to crystallographic substitution. For ionic substitution in crystals, there usually must be ionic size balance, charge balance and the numbers of ions must balance. For example, by substituting Na and La for Ca in $CaMoO_4$ there is a charge, size, and numbers balance[1] as follows:

$$2Ca^{2+} + 1Na^{1+} = 1La^{3+}$$

or

$$2CaMoO_4 \cong NaLa\,(MoO_4)_2$$

Because of these balanced substitutions, $NaLa(MoO_4)_2$ as well as $CaMoO_4$ can be grown as single crystals with the scheelite structure.

However, for ionic substitutions in the NRL core glass, only the numbers of ions and the charges were balanced. The ionic size of the substituted ion was either larger or smaller than the ion which was replaced. The goal was to either increase the refractive index of the core glass (larger substituted ions) or to decrease the ionic size for lower refractive indices for cladding glasses. Table 1 lists the ionic radii for various ions[2] in a number of different oxygen coordinations.

Na_2O and Al_2O_3 Substituted for CaO

Ionic charge and numbers balance with an overall decrease in ionic size in the NRL glass can be made by the following substitution:

$$4CaO = Na_2O + Al_2O_3$$

In other words, one mole of Na_2O and one mole of Al_2O_3 can be substituted for 4 moles of CaO in the NRL core glass and this should produce a decrease in refractive index.

Table II (a) lists these compositions (in mole %) and some glass properties. A N.A. has been calculated for a core glass with a refractive index of 1.58 and 1.62.

The refractive index decreased with decreasing CaO but for complete substitution of CaO there was some devitrification.

Na_2O, Al_2O_3 and MgO Substituted for CaO

One way to substitute Na_2O, Al_2O_3 and MgO for CaO in the core glass is shown below.

$$8CaO = Na_2O + Al_2O_3 + 4MgO$$

With this substitution there is a charge balance, a numbers balance and an average decrease in ionic size.

Table II (b) shows these compositions and some properties. There was a gradual decrease in n_D with decreasing CaO for this type of substitution.

MgO Substituted for CaO

The direct substitution of various amounts of MgO for CaO should produce lower indices of refraction with increasing amounts of MgO.

Table II (c) itemizes some properties and the compositions. There was a gradual decrease in n_D for increasing amounts of MgO. Complete substitution of MgO for CaO in the NRL core glass produced an opal glass.

MgO + Na_2O + B_2O_3 Substituted for CaO

MgO, Na_2O, and B_2O_3 were substituted for CaO as shown in Table II (d). This produced refractive indices lower than the NRL glass and lower annealing points and lower thermal expansions.

$Na_2O + SiO_2$ Substituted for CaO

Substitution of Na_2O and SiO_2 for CaO produced glasses with refractive indices lower than the NRL glass as shown in Table II(e).

$Na_2O + B_2O_3$ Substituted for CaO

Lower refractive indices were measured on glasses which had Na_2O and B_2O_3 substituted for CaO in the NRL base glass as shown in Table II(e).

1.2 Core Glass Modifications

With the present NRL core glass (n_D 1.58) a cladding class with a refractive index of about 1.46 is needed to produce a numerical aperture (N.A.) of 0.6. If the core glass had a $n_D = 1.62$ then the cladding glass would only need a $n_D = 1.504$ for a N.A. of 0.6. Consequently, a refractive index increase of the core glass might make the choice of a cladding glass somewhat easier. Therefore, ionic substitutions were made into the NRL core glass to increase ionic size with a subsequent increase in refractive index.

Y_2O_3 or SrO Substituted for Al_2O_3 or CaO

To increase the refractive index of the core glass, Y_2O_3 or SrO was substituted in different amounts (including complete substitution of SrO for CaO and complete substitution of Y_2O_3 for Al_2O_3).

Molar compositions and some properties are shown in Table III(a). Y_2O_3 proved to be much more effective in increasing the refractive index than did SrO. Four mole percent of Y_2O_3 increased the n_D from 1.58 to 1.615. Whereas complete substitution of SrO for CaO (29.7 mole %) only increased the n_D to 1.591.

Mixed substitution of Y_2O_3 and SrO for Al_2O_3 and CaO Table III(b) produced glasses with refractive indices almost identical to Y_2O_3 substitutions.

$Ca_3Al_2Si_2O_{12}$ to $Y_3Al_3O_{12}$ Glasses

Glasses in the $CaO-Al_2O_3 - Y_2O_3-SiO_2$ system were studied[3] in an earlier unrelated program. These are in effect a pseudo binary between $Ca_3Al_2Si_3O_{12}$ (CAS) and $Y_3Al_2Al_3O_{12}$ (YAG) and closer to CAS than YAG in composition. These were found to be stable glasses with high annealing points, low liquidus, high refractive indices and high thermal expansion. Compositions and properties are given in Table III(c).

NRL to CAS Series

A Series of glasses intermediate in composition to the NRL core glass and $Ca_3Al_2Si_3O_{12}$ were prepared and are listed in Table III(c). As the composition approached CAS and AP, SP, STP, n_D, α, and density all increased. The refractive index for CAS is 1.619.

La_2O_3 + SrO Substituted for Al_2O_3 & CaO; La_2O_3 for Al_2O_3

As shown in Table III(d), the refractive index was increased in glasses where La_2O_3 and SrO were substituted for Al_2O_3 and CaO. It was also increased when La_2O_3 was substituted for Al_2O_3.

Figure 1 is a graphic representation of n_D as a function of the various substitutions for CaO or Al_2O_3 in the NRL core glass. Also, in Figure 1, a guide for numerical aperature (N.A.) is presented which shows that a N.A. of 0.6 is not possible with these substitutions for a core glass with a refractive index of 1.60 or lower.

1.3 Selected Glasses

The core glasses selected were the NRL core glass and GS443. These have refractive indices of 1.58 and 1.60, respectively. Glasses GS442

and GS451 were the selected cladding glasses with GS454 and GS458 being second choices. The refractive indices of these four glasses are 1.529, 1.517, 1.517, and 1.510, respectively. Table IV shows the selected core and cladding glasses.

1.4 Appendices

Appendix A contains an equation for calculating the refractive index for glasses of limited composition. This equation was developed from 33 glasses, so statistically it is not very good. The coefficients for B_2O_3 and Na_2O are the most suspect.

Appendix B discusses a method for approximating the seal stress developed in sealing two different glasses together.

2. High Purity Raw Materials and Batch Preparation

2.1 High Purity Batch Materials

Early in Phase II, a comprehensive search was made to locate suppliers who could supply ultrapure chemicals for the batch ingredients required to make the final selected glasses. The primary concern for all chemicals was having iron as low as possible in order to achieve the low loss characteristics desired in the final glasses. Table V lists the chemicals obtained, the respective supplier and iron levels by in-house analyses.

2.2 Batch Preparation

Preparation of Clean Room & Equipment

The handling of raw materials and all batch preparation was carried our in a laminar, flow type clean room. This room was formerly accredited a Class 100 clean room but has not been monitored or accredited recently.

Before the room was used it was completely scrubbed (walls, floors & ceiling), the filters were inspected after which blowers were turned on. The air circulation system was run for one week prior to our move into the room.

After purging the room, all equipment that was to be used was thoroughly washed (tables, balances, etc.) and moved into the room. Plastic containers and other utensils were washed with warm soapy water and double rinsed with distilled water. They were then allowed to drain and air dry in the clean room.

Raw Materials

Upon receipt of all raw materials from suppliers they were placed in the clean room, then carefully sampled for analysis.

After receipt of analyses, batch calculations were made. Total batch weight was divided into suitable increments so that each batch charge was contained in one plastic container. This was done to prevent contamination of batch. The batch weighing was carried out by using only plastic scoops, funnels and utensils to transfer the material from container to balance. Materials were weighed into a plastic dish. After all ingredients were placed in the containers, each individual batch was rolled for 10 minutes on a jar mill for thorough mixing.

3. Melting

3.1 Melting of Improved Clad and Core Glasses

Melting of clad and core glass modifications were carried out using our "normal" purity batches and conventional melting techniques. These were described in detail in the Phase I report.

Additional melts of the final candidate cladding glasses (GS442 and GS451) and core glasses (NRL and GS443) were made for fabrication of small trial preforms. These glasses were batched using our normal purity batch materials and melted conventionally in a bottom cast furnace. The objective of bottom casting was to achieve better quality in the cast blanks. The blanks were then subsequentely core drilled and fabricated into the preform assemblies.

3.2 Melting in the Mini-Melter

Melting of the selected clad and core glasses were carried out in the mini-melter (Figure 2). Approximately 5 lbs. of glass was melted at a time. Four melts of GS443 core glass and one melt of clad glass GS442 were made. The initial melt in the mini-melter, GS443A5, was melted in air and samples cast to check out operation of the unit. The batch was prepared from our normal high-purity materials. The unit was then shut down because some foaming of the batch materials plugged the vent tubes. The platinum was reworked to locate both vent tubes through the crown and the seal wells were repaired. The unit was then cleaned, reinstalled and realigned.

Subsequent melts in the mini-melter were, in order, GS443A6, GS442A6, Gs443A7 and GS443A8. A summary of these melts is shown in Table VI.

After the last melt (GS443A8, the melter was dismantled. The seal wells were found to be leaking and a crack in the roof was found. These leaks in the sealed system were most likely the cause of the very slight or slight yellow color of the last three melts.

3.3 Other Melting

In a small side study, two small melts (150g and 100g) of GS443 core glass were made in an induction furnace under CO/CO_2 atmosphere. The glass batches were prepared from the very high purity raw materials. The resulting glasses were water white and one of them was subsequently analized analyzed for Fe_2O_3 at 1.4 and 1.7 ppm (two determinations).

At a later date, we decided to make an NRL core glass melt using the ultrahigh-purity materials. Prior to melting, the melter roof and seal wells were repaired. During melting, carastrophic failure occurred in the platinum melter bottom and seal wells. The platinum failure could be attributed to conditions in the previous melt(s), or more likely was a cumulative effect of the CO/CO_2 atmosphere and/or some possible residual organic material remaining in the MOD materials used in the high-purity batches.

The possibility that residual organic material in the MOD materials may have contributed (or caused) the platinum failure was indicated by some work unrelated to this contract. In that work, several crucible melts were made where the same ratio of CO/CO_2 gas was bubbled through the melt and also maintained above the melt. This melting was not a sealed system like the mini-melter. The same crucible was used for all of the melts and no deterioriation of the platinum was noted.

4. Preparation of Preform Assemblies and Fiber Drawing

All preforms were fabricated by core drilling tubes (clad glasses) and rods (core glasses) from small blocks of the appropriate glass. All longitudinal surfaces were then ground and polished.

4.1 Draw of Four Candidate Assemblies

Four small assemblies 5/8" O.D. x 3/8" I.D. x 6" long were fabricated from cladding glasses GS442 and GS451 and core glasses GS443 and NRL. The glasses for these assemblies were prepared from normal purity batch ingredients and were melted conventionally. The major objective of these draw trials was to observe compatability of core and clad glasses. The surface polish was not of good quality on the assemblies. Each of the assemblies were drawn in a single-step process (Figure 3) with the following results:

GS-442 Clad/NRL Core - Core glass softened ahead of clad glass (1650°F. and draw started, but clad glass too viscous. At 1720°F, draw was started but encountered numerous breaks. Only a small amount of fiber was obtained on the spool and this was without the Sylgard coating because of the difficulty in restringing. The fiber on the spool was very brittle and impossible to spool off without breakage. The brittleness may be due to the draw temperature being too low or the polish on the core rod not sufficiently good enough which resulted in very many microseeds at the interface.

GS-451 Clad/NRL Core - Core glass softened (1475°F) ahead of clad glass and began running out of tubing (1600°F). Clad glass pinched off and vacuum started. After draw started (1780°F) approximately 550 feet was collected when fiber broke. Restarted and remainder of fiber collected by coiling in a box. Fiber was somewhat brittle - broke several times while unwinding samples from the spool, but much improvement over above assembly.

GS-451 Clad/GS-443 Core - Core glass began to sag at 1360°F. Cladding pinched off at 1660°F and draw started at 1760°F. No problem with this draw. Collected approximately 1300 ft. on two spools.

GS-442 Clad/GS-443 Core - Core glass began sagging at 1340°F. Draw started at 1780°F. No problem with this draw. Collected approximately 1700 ft. on one spool.

With the exception of FS442 clad/NRL core, samples of the above fibers were sent to NRL for evaluation. NRL reported very poor transmission in the fibers. Subsequently, sample fibers (random 3-foot lengths) of GS442/NRL, GS442/GS443 and GS451/NRL were observed in a Leitz Petrographic Microscope. All samples showed elongated seeds at the interface. Cross sections of the assembly root showed masses of seeds at the interface of the core and clad. SEM showed all three samples of core and cladding had pits and gouges. These were observed on the polished outside surfaces of the core rod and inner surfaces of the clad. Both core rod and cladding surfaces showed possible grinding and/or polishing materials within these pits and gouges. During the course of the above work, no devitrification was seen in any of the above fibers. The obvious conclusion of this study was that the grinding and polishing technique for perparing the core rods and clad tubing was inadequate to produce a high-quality fiber.

4.2 Draw of Final Glass Assemblies

Two assemblies, 5/8" O.D. x 3/8" I.D. x 7" long were prepared from clad glass GS442 Melt 6 and core glass GS443 Melt 6 that were melted in the min-melter (see Section 3.2, page 13). Examination of the finished surfaces indicated they were not adequate to produce a good fiber, i.e., one having a good interface. Acid washing (four second

dip in a $HF-H_2SO_4-H_2O$ solution) of one of the two assemblies was unsatisfactory. The resulting surfaces, after acid washing of the core and clad, were worse than the original polished surfaces as shown by microscopic examination. These examinations showed what appeared to be innumerable small seeds or particles of devitrification in the core glass (GS443). Electron micrographs confirmed the presence of seeds (not devitrification) on the order of 1/3 micron in size. However, EM (Electron Micrographs) did show the presence of structure in the core glass which was concluded to be phase separation. Electron micrographs did not show phase separation in the GS442 melt 6 clad glass. Electron micrographs of GS442 Melt 5, GS443 melt 2, and NRL melt 11, which were melted conventionally and subsequently drawn to fiber in March 1980 (4.1 draw of four candidate assemblies) did not show any micro structure. Althrough not confirmed, a reasonable explanation might be the higher B_2O_3 content (almost on target composition) of the glasses melted in the mini-melter. The mini-melter is a closed system as compared to the conventional melting in open pots in which the earlier melts were made.

The acid etched assembly described above was subsequently repolished, with special effort to obtain the best polish possible with in-house capabilities. The resulting finish, although less than desired, was much improved over the initial polish. This assembly was cleaned in an ultrasonic bath and then redrawn into fiber. Approximately 2300 ft. of fiber was collected on three spools. Fiber diameter was ≈ .005" with the exception of the last ≈450 ft. on dpool #3 which was .010" diameter. Spools 2 and 3 (total of ≈1100 ft.) were sent to NRL.

5. NRL Evaluation of Test Fibers

The NRL evaluation of the test fibers was inconclusive due to the brittleness and poor transmission of the fibers. O-I believes the brittleness and poor transmission were primarily due to the poor interface between the clad and core glasses. Our problems in obtaining a good polish on the mating surfaces were outlined in Section 4. The preform assembly parts were just too small to polish properly. The brittleness may have been accentuated by the large thermal expansion difference between the clad and core glass.

In recent work, unrelated to this contract, concerning the evaluation of the NRL glass for scintillation counters, it was determined that we could produce large, water white rods of the size we normally supply to Collimated Holes, Inc. Commercially available N51A Kimble tubing was used as a clad glass. Dick Mead of Collimated Holes was able to draw what he described as good looking and strong waveguides.

	NRL	N51A
SP (°C.)	820	785
AP (°C.)	677	575
STP (°C.)	636	530
n_D	1.58	1.50
α_e (10^{-7}/°C.)	60.9	55
α_c (10^{-7}/°C.)	83.4	74
N.A./1.58		0.50

The outside surface of the cast rod and the inside surface of the drawn tubing were in better condition without polishing than any of the preform assemblies were after polishing. Also, the thermal expansion mismatch is more reasonable with a calculated stress of 1000 to 1500 psi compression in the N51A clad.

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3. E. A. Weaver, "Some Glasses and Properties in the CaO-Al O - Y O -SiO System," unpublished results.

VI. GLOSSARY OF SYMBOLS AND TERMS

SP (°C.)	Glass softening point (viscosity = $10^{7.6}$ poises)
AP (°C.)	Annealing point (viscosity $10^{13.36}$ poises)
STP (°C.)	Strain point (viscosity = $10^{14.6}$ poises)
n_D	Refractive index at NaD line (589.3 nm)
$\alpha_E(10^{-7}/°C.)$	Thermal expansion coefficient (0-300°C.)
$\alpha_C(10^{-7}/°C.)$	Thermal contraction coefficient (AP-25°C.)
$\rho(g/cm^3)$	Density
N.A./1.58	Numerical Aperature = $\sqrt{n_1^2-n_2^2}$ for core glass with n_D of 1.58 (n_1 = 1.58)
n_1	Core glass refractive index
n_2	Cladding glass refractive index
Gradient (4h)	Glass stability test where about $(6\ mm)^2$ x 15 cm bars of glass are heated in Pt boats in a temperature gradient (625°C-1000°C) for (4h) or (16h). Examined for opalescence or devitrification.
Color	Visual color of glass
Seal Test	Test where bars of glass (6 mm x 6 mm x 2 cm) sealed together at 875°C for 2 hrs. Seals given visual and polaroscopic examination.

Table I

Sizes of Ions Used in

Cladding and Core Glasses

Ion	CN*	Radius (°A)	Ion	CN*	Radius (°A)
Al^{3+}	IV	0.53	O^{2-}	IV	1.24
	VI	0.67		VI	1.26
B^{3+}	III	0.16		VIII	1.28
	IV	0.26	Si^{4+}	IV	0.40
Ba^{2+}	VI	1.5		VI	0.54
	VIII	1.56	SR^{2+}	VI	1.27
	X	1.66		VIII	1.39
	XII	1.74		X	1.46
Ca^{2+}	VI	1.14		XII	1.54
	VIII	1.26	Y^{3+}	VI	1.04
	X	1.42		VIII	1.155
	XII	1.49			
Ce^{3+}	VI	1.15			
	VIII	1.28			
	XII	1.43			
Ce^{4+}	VIII	1.11			
K^{1+}	VI	1.52			
	VIII	1.65			
	X	1.73			
Mg^{2+}	IV	0.72			
	VI	0.86			
	VIII	1.03			
Na^{1+}	IV	1.13			
	VI	1.16			
	VIII	1.30			

* CN = Coordination Number

Table II(a)

CLAD MODIFICATIONS

Na_2O & Al_2O_3 for CaO

(Moles)

	NRL	GS-412	GS-413	GS-414	GS-415	GS-450 *	GS-451	GS-452	GS-416
SiO_2	4.06	4.06	4.05	4.06	4.06	4.05	4.04	4.03	4.03
CaO	2.45	2.12	1.86	1.59	1.33	0.97	0.63	0.31	-
Al_2O_3	0.70	0.78	0.85	0.92	0.98	1.07	1.15	1.23	1.31
B_2O_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CeO_2	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.04	0.04
Na_2O	-	1.08	0.15	0.22	0.28	0.37	0.45	0.53	0.61
SP(°C.)	820			810	822	844	868	l.devit.	devit
AP(°C.)	677			652	649	641	648		
STP(°C.)	636			611	608	594	595		
n_D	1.58	1.571	1.561	1.559	1.547	1.529	1.517	1.507	1.498
$\alpha_e(10^{-7}/°C.)$	60.9			54.7	53.0	51.7	49.3	≈45	
$\alpha_c(10^{-7}/°C.)$	83.4			74.9	73.7	69.7	66.5	≈64	
$\rho(g/cm^3)$	2.69	2.61	2.575	2.53	2.51		2.430	0.475	2.34
N.A./1.58		0.14	0.24	0.26	0.32	0.4	0.44	0.54	0.5
N.A./1.60		0.24	0.35	0.36	0.41	0.47	0.51		0.56
Gradient(4h) 625°C. to 1000°C.	stable			stable	stable	stable	very stable	opaque bands	devit. band 725-875
Gradient(16h)						l.devit >875°C.	stable		
Color	clear	clear	clear	clear	clear	vl amber	vl amber		l.amber
Seal 875°C.(2h)									
to NRL Core					good	good	good	good	
to GS-443						good	good	good	

* 1/22/80 telephone report by Bob Ginther, "Remelted GS-450 sample 2 hrs. in 75% CO-25% CO_2 atmosphere and resulting glass achieved water white characteristics. No redox problem."

Table II(b)

CLAD MODIFICATIONS

MgO, Al_2O_3 & Na_2O for CaO

(Moles)

	NRL	GS-417	GS-418	GS-419	GS-420	GS-441	GS-442*	GS-421
SiO_2	4.06	4.06	4.06	4.06	4.05	4.05	4.05	4.04
CaO	2.45	2.12	1.80	1.49	1.17	0.77	0.38	-
Al_2O_3	0.70	0.74	0.78	0.82	0.86	0.91	0.96	1.0
B_2O_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CeO_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
MgO	-	0.16	0.32	0.48	0.64	0.84	1.03	1.22
Na_2O	-	0.04	0.08	0.12	0.16	0.21	0.26	0.31
SP(°C.)	820				826		835	860
AP(°C.)	677				659		648	663
STP(°C)	636				616		601	613
n_D	1.58	1.575	1.565	1.559	1.551	1.541	1.529	1.523
$\alpha_e(10^{-7}/°C.)$	60.9				63.1		47.1	44.0
$\alpha_c(10^{-7}/°C.)$	83.4				70.6		65.4	62.5
$\rho(g/cm^3)$	2.6927	2.68	2.64	2.61	2.58	2.57	2.483	2.51
N.A./1.58		0.12	0.22	0.26	0.3	0.35	0.4	0.42
N.A./1.60		0.29	0.34	0.36	0.4	0.43	0.47	0.49
Gradient(4h) 625°C. to 1000°C.	stable				stable	stable	v. stable	vl. devit. >925°C.
Gradient(16h)	vl.devit. >875°C.						stable	l. devit. >925°C.
Color	clear	clear	clear	clear	clear	clear	clear	clear
Seal 875°C.(2h) to NRL Core to GS-443 & GS-433					good	good	good interface cracks	inter-face cracks

v = very
l = light
* 1/22/80 telephone report by Bob Ginther, "Remelted GS-442 sample, 2 hrs. in 75% and 25% CO_2 atmoshpere and resulting glass achieved water white characteristic. No redox problem.

Table II(c)
CLAD MODIFICATIONS
MgO for CaO
(Moles)

	NRL	GS-422	GS-423	GS-424	GS-425	GS-426
SiO_2	4.06	4.06	4.06	4.06	4.06	4.06
CaO	2.45	2.15	1.82	1.49	1.16	-
Al_2O_3	0.70	0.70	0.70	0.70	0.70	0.70
B_2O_3	1.0	1.0	1.0	1.0	1.0	1.0
CeO_2	0.05	0.05	0.05	0.05	0.05	0.05
MgO	-	0.31	0.64	0.97	1.30	2.45
Na_2O						
SP(°C.)	820			820	838	
AP(°C.)	677			670	679	
STP(°C)	636			628	635	
n_D	1.58	1.577	1.571	1.567	1.563	
$\alpha_e(10^{-7}/°C.)$	60.9			53.6	50.7	
$\alpha_c(10^{-7}/°C.)$	83.4			72.3	69.6	
$\rho(g/cm^3)$	2.69	2.69	2.67	2.65	2.65	2.54
N.A./1.58		0.08	0.17	0.2	0.23	
N.A./1.60		2.275	0.31	0.34	0.345	
Gradient(4h) 625°C.-1000°C.					vl. devit. >900°C.	
Gradient(16h)						
Color	clear	clear	clear	clear	clear	opal
Seal 875°C.(2h) to NRL Core to GS-443 & to GS-433						

Table II(d)

CLAD MODIFICATIONS

$MgO + Na_2O_3 + B_2O_3$ for CaO*

(Moles)

	NRL	GS-453	GS-455	GS-454
SiO_2	5.78	5.78	5.77	5.78
CaO	3.49	2.27	1.10	-
Al_2O_3	1.0	1.0	1.0	1.0
B_2O_3	1.42	1.58	1.72	1.86
CeO_2	0.07	0.07	0.07	0.07
MgO	-	0.61	1.19	1.75
Na_2O	-	0.15	0.30	0.44
SP(°C.)	820		812	822
AP(°C.)	677		639	636
STP(°C.)	636		598	593
n_D	1.58	1.56	1.538	1.517
$\alpha_e(10^{-7}/°C.)$	60.9		48.9	46.2
$\alpha_c(10^{-7}/°C.)$	83.4		70.2	64.0
$\rho(g/cm^3)$	2.69		2.54	
N.A./1.58		0.25	0.36	0.44
N.A./1.60		0.36	0.44	0.51
Gradient(4h) 625°C. to 1000°C.			stable	
Gradient(16h)				1. opalescence 710-780°C.
Color	Clear		Clear	
Seal 875°C.(2hrs.)				
to NRL Core			good	good
to GS-443 & to GS-433			good	good

* Note the mole ratio uses Al_2O_3 as base rather than B_2O_3.

Table II(e)

CLAD MODIFICATIONS

		Na_2O_3& SiO_2 for CaO (Moles)		$Na_2O + B_2O_3$ for CaO (Moles)		
	NRL	GS-445	GS-446	GS-447	GS-458	GS-448
SiO_2	5.78	6.19	6.95	5.78	5.79	5.79
CaO	3.49	2.27	-	2.27	0.70	0
Al_2O_3	1.0	1.0	1.0	1.0	1.0	1.0
B_2O_3	1.42	1.43	1.43	1.73	2.12	2.30
CeO_2	0.07	0.07	0.06	.07	0.06	0.06
Na_2O	-	0.41	1.17	0.31	0.70	0.87
SP(°C.)	820					
AP(°C.)	677					
STP(°C.)	636					
n_D	1.58	1.549	1.493	1.553	1.510	1.487
$\alpha_e(10^{-7}/°C.)$	60.9					
$\alpha_c(10^{-7}/°C.)$	83.4					
ρ (g/cm^3)						
N.A./1.58		0.31	0.52	0.29	0.45	0.535
N.A./1.60		0.4	0.57	0.39	0.52	0.59
Gradient(4h) 625°C. to 1000°C.		stable	opal band 679-910°C.	stable	stable	opaque band 875-920°C.
Gradient(16h)						
Color		clear	amber	clear	clear	l. amber
Seal 875°C.(2h) to NRL Core to GS-443 & GS-433			 opalized		 good good	

Table III(a)

CORE MODIFICATIONS

	SrO for CaO (Moles)			Y_2O_3 for Al_2O_3 (Moles)			
	NRL	GS-431	GS-432	GS-427	GS-428	GS-429	GS-430
SiO_2	4.06	4.06	4.06	4.06	4.06	4.06	4.06
CaO	2.45		1.23	2.45	2.45	2.45	2.45
Al_2O_3	0.70	0.70	0.70	0.54	0.37	0.21	-
B_2O_3	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CeO_2	0.05	0.05	0.05	0.05	0.05	0.05	0.05
SrO	-	2.45	1.23				
Y_2O_3	-			0.17	0.33	0.50	0.70
La_2O_3							
SP (°C.)	820		805			*	
AP(°C.)	677		667			702	
STP(°C.)	636		626			662	
n_D	1.58	1.591	1.585	1.602	1.615	1.633	1.657
$\alpha_e(10^{-7}/°C.)$	60.9		65.6			73.0	
$\alpha_c(10^{-7}/°C.)$	83.4		86.5			90.9	
$\rho(g/cm^3)$	2.6927	3.21	2.92	2.79	2.94	3.06	3.26
Gradient (4h) 625°C.-1000°C.	stable	stable		l. devit. > 875°C.	l. devit. > 850°C.		h. devit. > 850°C.
Gradient (16h)				m. devit. > 875°C.			
Color	clear	clear	clear	clear	clear	clear	clear

h = heavy

* = Couldn't draw fiber

Table III(b)

CORE MODIFICATIONS

Y_2O_3 & SrO for Al_2O_3 and CaO

(Moles)

	NRL	GS-433	GS-434	GS-435	GS-436
SiO_2	4.06	4.06	4.06	4.06	4.06
CaO	2.45	1.83	1.21	0.60	-
Al_2O_3	0.70	0.54	0.37	0.21	-
B_2O_3	1.0	1.0	1.0	1.0	1. 0
CeO_2	0.05	0.05	0.05	0.05	0.05
SrO	-	0.62	1.24	1.86	2.45
Y_2O_3	-	0.17	0.33	0.50	0.70
SP(°C.)	820	848	828	838	
AP(°C.)	677	697	689	698	
STP(°C.)	636	655	547	656	
n_D	1.58	1.605	1.619	1.637	1.659
$\alpha_e(10^{-7}/°C.)$	60.9	67.2	70.9	77.0	
$\alpha_c(10^{-7}/°C.)$	83.4	87.1	91.4	97.0	
$\rho(g/cm^3)$	2.6927		3.20	3.40	3.69
Gradient(4h) 625°C. - 1000°C.		vvl. devit. >915°C.	l. devit >875°C.	m. devit. >850°C.	
Gradient(16h)		m. devit. >875°C.			
Color		Clear	Clear	Clear	Clear

Table III(c)

CORE MODIFICATIONS

	CAS-YAG (Mole%)					NRL-CAS (Mole %)			
	CAS440	B	C	D	NRL	GS-437	GS-438	GS-439	GS-440
SiO_2	42.86	40.74	38.46	36.0	49.1	47.54	45.98	44.42	42.6
CaO	42.86	40.74	38.46	36.0	29.7	32.99	36.28	39.57	42.6
Al_2O_3	14.29	16.67	19.23	22.0	8.5	9.95	11.40	12.84	14.2
B_2O_3					12.1	9.08	6.05	3.03	-
CeO_2		0.14	0.14	0.14	0.6	0.6	0.6	0.6	0.6
Y_2O_3		1.85	3.84	6.0					
% CAS	100	95	90	84	0	25	50	75	100
SP (°C.)	920	934	948	964	820			880	920
AP(°C.)	788	797	811	820	677			731	788
STP(°C.)	766	771	796	797	636			690	766
n_D	1.619	1.6280	1.6396	1.6496	1.58	1.591	1.599	1.611	1.619
$\alpha_e(10^{-7}/°C.)$	71.7	70.2	68.6	66.9	60.9			71.0	71.7
$\alpha_c(10^{-7}°C.)$					83.4			87.3	
$\rho(g/cm^3)$	2.894	2.957	3.042	3.133	2.6927	2.75	2.8	2.83	2.894
Gradient (4h) 625°C. to 1000°C.	stable								stable
Gradient (16h)									
Color	l. amber					clear	clear	clear	l. amber

Table III(d)

CORE MODIFICATIONS

			La$_2$O$_3$ & SrO for Al$_2$O$_3$ & CaO (Moles)			La$_2$O$_3$ for Al$_2$O$_3$
	NRL	GS-457	GS-443	GS-444	GS-456	GS-449
SiO_2	4.06	4.06	4.06	4.06	4.06	4.06
CaO	2.45	1.96	1.83	1.21	0.60	2.45
Al_2O_3	0.70	0.55	0.54	0.37	0.21	0.37
B_2O_3	1.0	1.0	1.0	1.0	1.0	1.0
CeO_2	0.05	0.05	0.05	0.05	0.05	0.05
SrO		0.50	0.62	1.24	1.86	-
La_2O_3		0.15	0.17	0.33	0.50	0.33
SP(°C.)	820	813	814	815		
AP(°C.)	677	672	673	678		
STP(°C.)	636	633	632	638		
n_D	1.58	1.605	1.607	1.630	1.653	1.628
$\alpha_e(10^{-7}/°C.)$	60.9	67.6	67.6	73.9		
$\alpha_c(10^{-7}/°C.)$	83.4	88.6	89.1	95.3		
$\rho(g/cm^3)$	2.6927	2.9724	3.05	3.31		
Gradient (4h) 625°C. to 1000°C.			stable	m. devit. >825°C.		
Gradient (16 hr)		1. devit. >840°C.	1. devit. >825°C.			
Color			Clear	Clear		

Table IV

Selected Glasses (m%)

	NRL	GS-443	GS-442	GS-451
SiO_2	49.1	49.1	52.39	55.2
CaO	29.7	22.2	4.9	8.62
Al_2O	8.5	6.5	12.38	15.74
B_2O_3	12.1	12.1	12.94	13.65
CeO_2	0.6	0.6	0.6	0.6
SrO	-	7.5	-	
La_2O_3	-	2.0	-	
MgO	-		13.37	
Na_2O			3.35	6.19
SP(°C.)	820	814	835	868
AP(°C.)	677	673	648	648
STP(°C.)	636	632	601	595
n_D	1.58	1.607	1.529	1.517
$\alpha e(10^{-7}/°C.)$	60.9	67.6	47.1	49.3
$\alpha c(10^{-7}/°C.)$	83.4	89.1	65.4	66.5
$\rho(g/cm^3)$	2.6927	3.05	2.483	2.430
N.A./1.58	-	-	0.4	0.44
N.A./1.60	-	-	0.47	0.51

Table V

NRL RAW MATERIALS

Raw Material	Supplier	Iron Content (ppm)
MOD Silica	Owens-Illinois, Inc.	0.2
MOD Alumina	Owens-Illinois, Inc.	1-3
MOD Boric Acid	Owens-Illinois, Inc.	0.1
Magnesium Oxide S54548G	United Mineral & Chemical	1-2
Magnesium Carbonate H1001	Ultra Pure Chemicals	0.2
Sodium Carbonate 1001	Ultra Pure Chemicals	0.4
Cerium Oxide R1623	United Mineral & Chemical	1
Lathanum Oxide R1397	United Mineral & Chemical	0.4
Strontium Carbonate	Ultra Pure Chemicals	0.2
Sodium Chloride 914134	J. T. Baker (Ultrex)	0.7
Calcium Flouride C-1500	Ultra Pure Chemicals	0.8
Calcium Carbonate C-1002	Ultra Pure Chemicals	0.2
Calcium Carbonate 905233	J. T. Baker (Ultrex)	0.02

Table VI

SUMMARY OF MELTS MADE IN MINI-MELTER

	Core GS-443 A5	Core GS-443 A6	Clad GS-442 A6	Core GS-443 A7	Core GS-443 A8
Melt Temp. (°F.)	2850	2850	2850	2850	2850
Casting Temp. (°F.)	2800	2700	2900	2700	2700
Melting Time (hrs.)	29	28	30	28	28
Stirring Time (hrs.)	21	24	23	24	23
Stirring (rpm)	70-30-20	40-20	40-20	40-20	40-20
Atmosphere	Air	CO/CO_2*	CO/CO_2*	CO/CO_2*	CO/CO_2*
Gas Flow Rate(CFH)	-	1.0	1.0	1.0	1.2
Type of Batch	Normal	Normal	Normal	High Purity	Normal
Glass Color	Yellow	Water White	Very Sl. Yel.	Sl. Yel.	Very Sl. Yel.
Calculated Fe_2O_3(ppm)	4	4	6	<1	4
Chemical Analysis					
B_2O_3 (Wt.%)	11.54	11.14			
Fe_2O_3 (ppm)	8	8			

* 75%CO/25%CO_2

FIGURE 1. Refractive Index as a Function of Mole % CaO or Al_2O_3 Replaced by Other Oxides in NRL Core Glasses

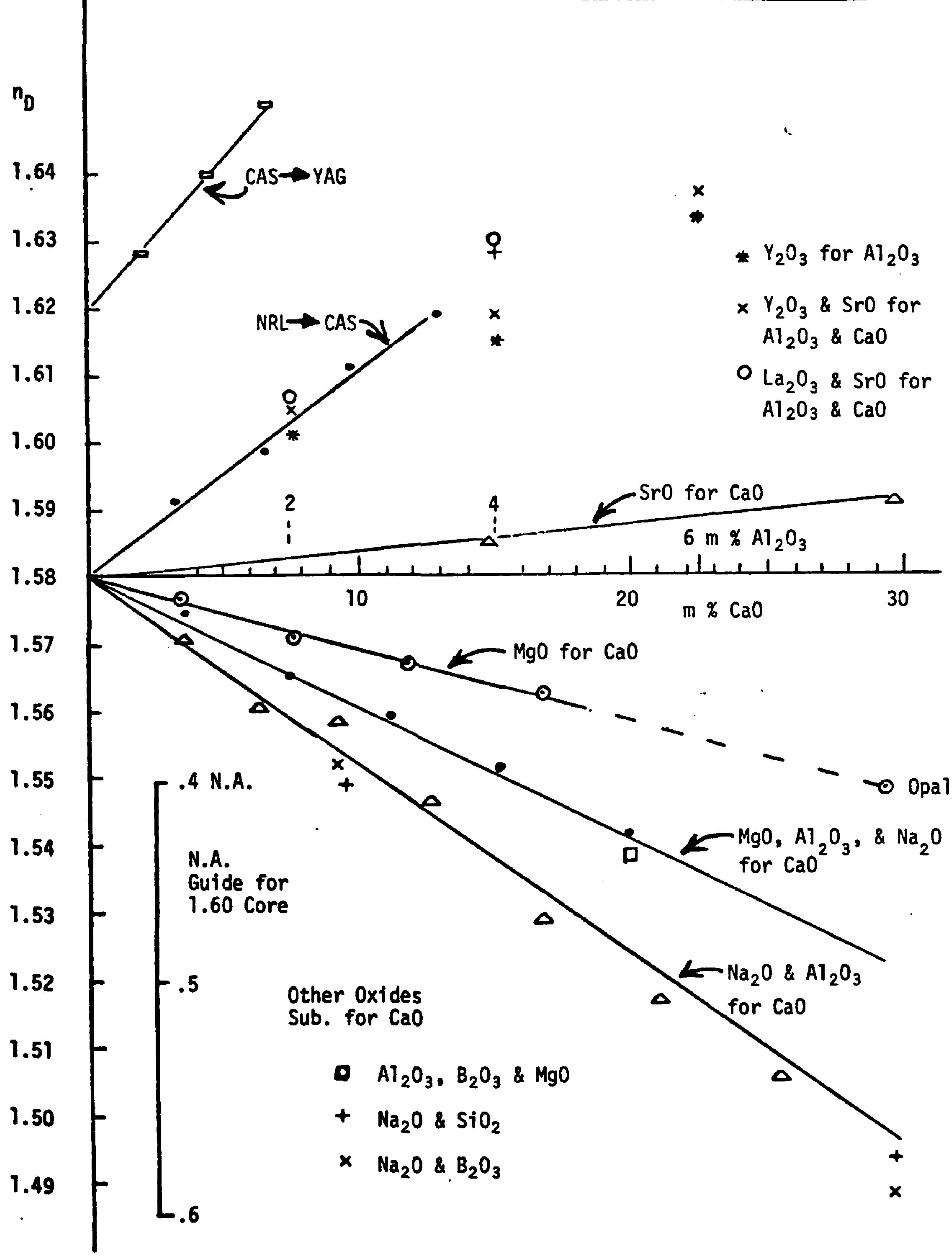


FIGURE 2. Mini-Melter

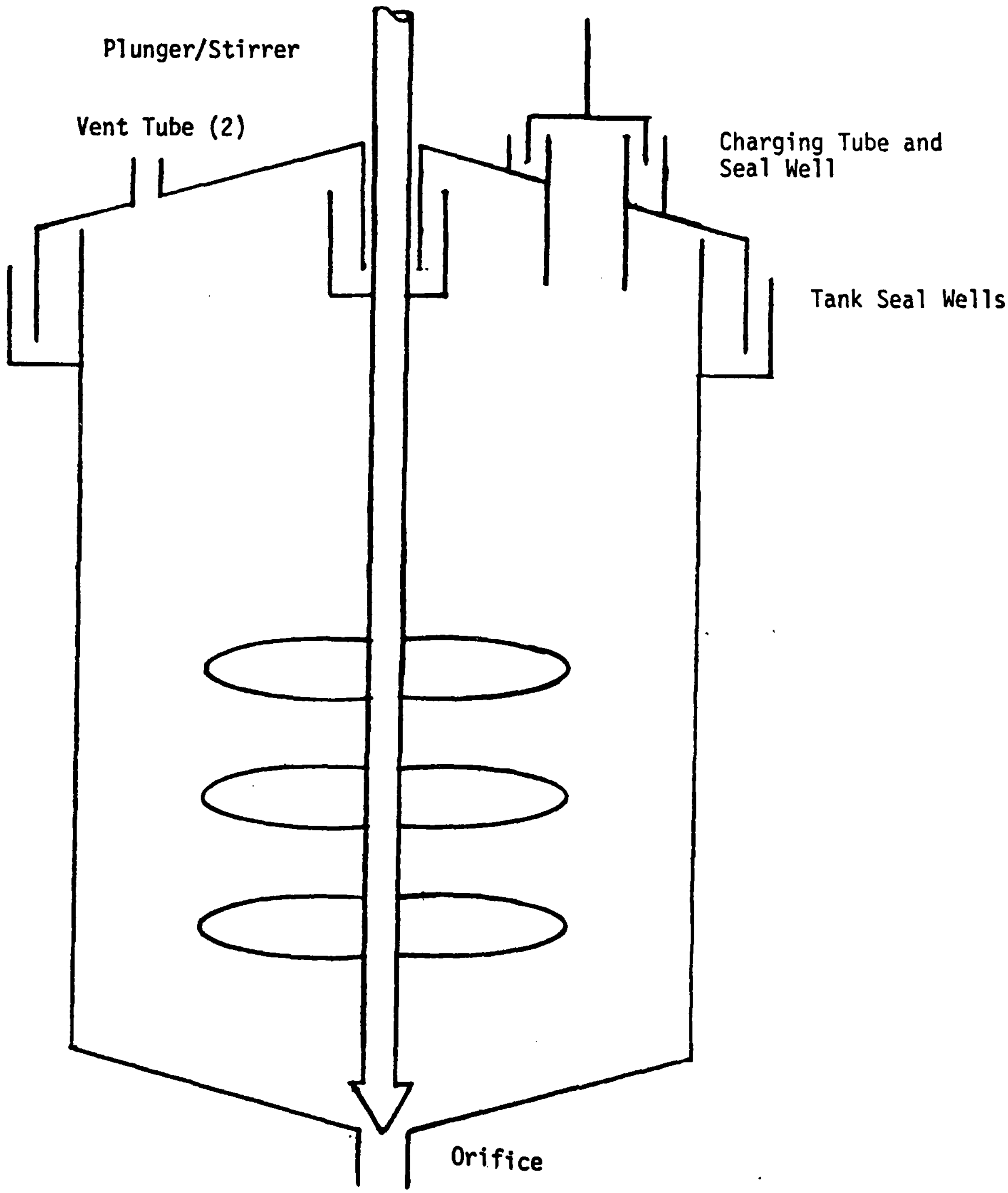
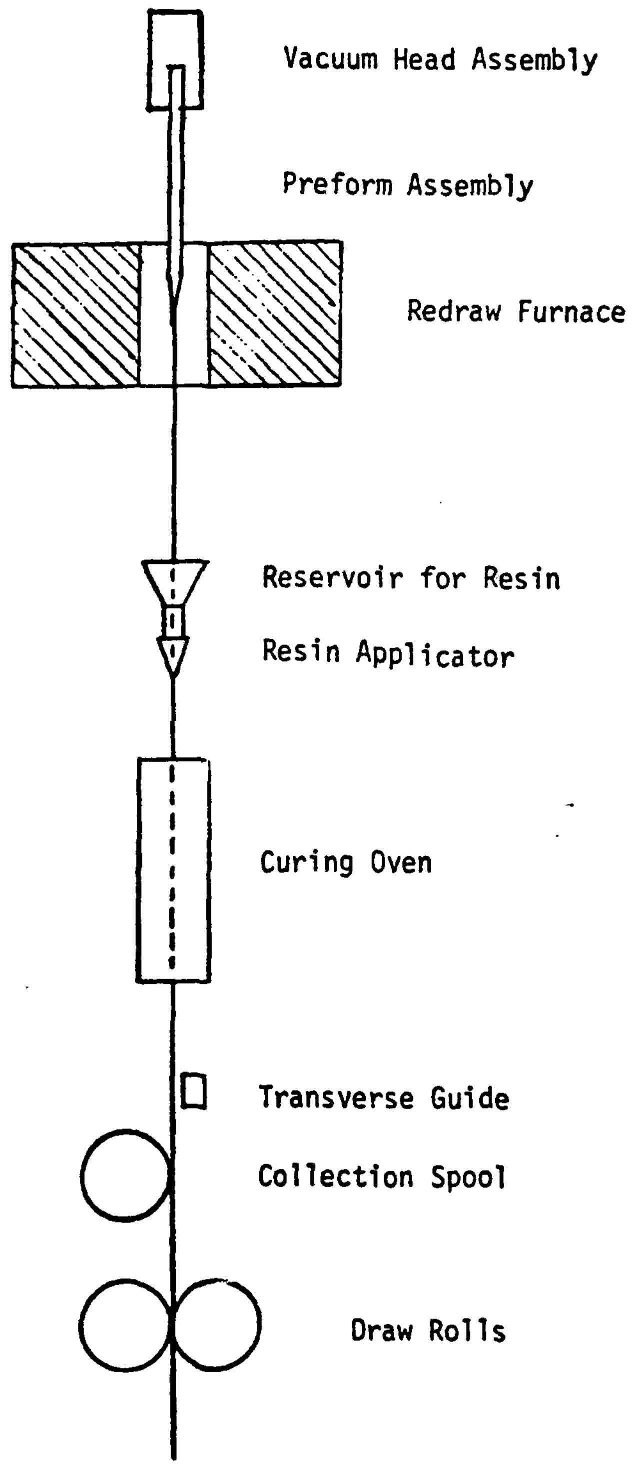


FIGURE 3. Redraw Arrangement



APPENDIX A

An Equation for Calculating the Refractive Index of Certain Glasses for NRL

A linear correlation equation {of the form n_D = a (mole % SiO_2 + b (mole % CaO) + . . . } has been generated which relates the refractive index of glasses to their composition. The equation coefficients, presented in the following Table, were developed from a total of 33 experimental melts containing a total of nine different oxides. The first column of the table lists the nine oxides which were present in the glasses. The second column gives the coefficient which is to be multiplied by the amount of the oxide indicated in the first column. The compositions of all the glasses used in this work were the target compositions expressed in mole %.

The values in column three indicate the numerical accuracy which can be associated with the coefficients. Column four lists the non-zero amounts of the oxides used in this study.

APPENDIX A (CONTINUED)

Oxide Term	Coefficient	95% Confidence Limit of Coef.	Non-Zero Oxide Amounts (m %)
SiO_2	.00869	.0068	35.95 - 57.66
CaO	.0241	.0068	7.2 - 42.86
Al_2O_3	.0149	.00027	2.5 - 21.97
B_2O_3	.0249	.0109	3.02 - 14.32
CeO_2	.0165	.0069	0.14 - 0.64
Na_2O	.0401	.0271	0.5 - 8.72
MgO	.0228	.0068	2.01 - 16.05
Y_2O_3	.0235	.0031	1.84 - 8.5
SrO	.0243	.0068	7.46 - 29.7

APPENDIX B

Calculated Stress

It would be of interest to know the difference in thermal expansion or stress between core glass and cladding glass which can be tolerated. According to Corning's patent[1] on their Corelle dinnerware two examples are tabulated below:

	1	2
Core α (10^{-7}/°C.)	94.0	67.0
Clad α (10^{-7}/°C.)	46.0	46.0
Core thickness (in.)	0.080	0.070-0.090
Clad thickness (in.)	0.002	0.003
$\Delta\alpha$	48.0	21
Thickness ratio (core to clad)	20:1	12:1 to 15:1

As further background, a typical stress developed in air tempered glass[2] is about 20,000 compression psi. This surface stress is contained in about 20% on each side of a plate while the 60% of the interior has the balancing tensile stress.

Approximate seal stress can be calculated[3] from thermal contraction curves as follows:

(1) Subtract 15°C. from lowest annealing point of core or cladding glass

(2) Find $\Delta L/L$ from contraction data for each glass at temperature from (1)

(3) Take difference in $\Delta L/L$ values ($\Delta L/L - \Delta L/L$)

(4) Multiply differences in $\Delta L/L$ (3) by 50. This value is the

approximate seal stress in psi.

Some samples of calculated stress are listed below:

	1 AP	AP-15°C	Clad 3 ΔL/L@2	NRL Core 4 ΔL/L@2	4-3	Stress in Clad Δx50 (psi)
GS-442	648	633	370	436	66	3300C
GS-451	648	633	385	436	51	2500C
GS-442	648	633	370	470(GS443 core)	100	5000C
GS-451	648	633	385	470(GS443 core)	85	4250C

References

1. U. S. Patent 3,673,049
2. Private communication
3. Private communication

END

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